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Short Communication

Oxidation of 5-hydroxymethylfurfural to 2,5-diformylfuran with molecular oxygen in the presence of N-hydroxyphthalimide

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ABSTRACT

Catalytic system $Cu(NO_3)_2$/NHPI can be successfully used for the mild oxidation of 5-hydroxymethylfurfural (HMF) to 2,5-diformylfuran with molecular oxygen. The oxidation reaction takes place at 50 °C and 1 atm O_2 and selectively converts the primary hydroxymethyl group of HMF to the aldehyde one. The selective formation of aromatic aldehyde is observed because of the higher rate of hydrogen abstraction from primary alcohols by the phthalimide-N-oxyl radical, as compared to the rate of the hydrogen abstraction from the aldehydes.

1. Introduction

The carbohydrates of plant tissues are the major biofeedstocks of organic chemicals that can replace those derived from petrochemical sources. Thermal dehydration of hexoses in acidic media gives 5-hydroxymethylfurfural (HMF), which has high industrial potential as a chemical intermediate. The selective oxidation of the hydroxymethyl group leads to the formation of furanic dialdehyde — 2,5-diformylfuran (DFF). Various applications of DFF have been described [1,2], including its use as a monomer for important furan-containing polymers and materials with special properties [3–8]. Traditionally, DFF has been prepared from HMF by oxidation with stoichiometric amounts of inorganic oxidants [9–13], but these methods are expensive and result in large amounts of inorganic salts as waste. Processes with inorganic oxidants often suffered from low selectivity, and it is not easy to oxidize solely hydroxymethyl moiety to produce aldehyde. It is known that the aerobic oxidation of primary alcohols, catalyzed by N-oxyl radicals — 2,2,5,5-tetramethylpiperidine-N-oxyl (TEMPO) [14–16] and phthalimide-N-oxyl (PINO) [17–19] combined with transition metal salts, proceeded smoothly and gave aldehyde as the main product. Transition metal ions, such as Co(II), Mn(II), Cu(I), and Cu(II) are typically used as co-catalysts in these oxidation processes, catalyzed by N-hydroxyphthalimide.

Herein, we describe an efficient oxidation of HMF to DFF in the presence of catalytic systems based on NHPI, utilizing dioxygen as the oxidant.

2. Experimental

2.1. Materials

N-hydroxyphthalimide was purchased from Fluka and used as received. HMF was synthesized from fructose as described [20]. Iodobenzenediacetate ($PhI(OAc)_2$) and copper nitrate trihydrate were synthesized as described in [21,22]. Acetonitrile was Merck “gradient grade for liquid chromatography”. The substituted N-hydroxyphthalimides were synthesized according to modified literature procedures [23]. Other chemicals were purchased and used without prior purification.

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2.2. Methods

Oxidation kinetics was studied at constant oxygen pressure (1 atm) with the gas-volumetric method (Supporting information, Fig. S1) by measuring the volume of the absorbed oxygen. Intensity of agitation of a reaction vessel was enough to conduct reaction in the kinetic regime. The initial reaction rates were calculated from the slope of the linear plots of the $[O_2]$ consumed vs. time. All kinetic experiments were carried out by using freshly prepared samples.

Rate constants of H-abstraction from furan compounds (RH) by PINO were measured in acetonitrile by UV–vis spectrophotometry, using Analytic Jena SPECORD S300 equipped with a thermostated cell holder. PINO was generated by the oxidation of NHPI (7.15×10^{-3} M) with $PhI(OAc)_2$ (7.15×10^{-4} M) in deoxygenated acetonitrile. The PINO formation was followed by the intensity of a peak at $\lambda_{max} = 382$ nm. The PINO concentration decreases by first order kinetics ($k_d = 0.5 \times 10^{-3}\ s^{-1}$ in MeCN at 25 °C). A solution of the furan compound was added into the PINO solution in the cuvette ([RH] varied in the range 3.9×10^{-3}–7×10^{-3} M) and the absorbance change was monitored at 382 nm (Supporting information, Figs. S2–S4). The decay of PINO strongly accelerated in the presence of a substrate. The kinetics were nicely described by Eq. (1):

$$\ln \frac{(A_t - A_\infty)}{(A_o - A_\infty)} = -(k_d + 2k_H[RH])t \qquad (1)$$

where A_t is the time dependent absorbance, A_0 and A_∞ are the absorbances at t = 0 and t = ∞, respectively, k_d is the first-order rate constant for spontaneous decay of PINO (s^{-1}) and k_H is the second-order rate constant for hydrogen abstraction from RH ($M^{-1} \cdot s^{-1}$).

The factor 2 before k_H indicates that the recombination reaction of a carbon-centered radical (R) with PINO leads to an adduct PINO–R formation. Second-order rate constants k_H were obtained from the plot of the observed rate constant k_{obs} vs. the substrate concentration.

EPR spectra were recorded on EPR spectrometer CMS8400, and induction modulation frequency of the polarizing field is 100 kHz. Magnetic parameters were measured by field calibration with the DPPH radical (g = 2.0036). The EPR spectrum of PINO (g = 2.0073) is obtained by adding copper(II) nitrate to a solution of NHPI in acetonitrile with Mn(II) in MgO as an internal standard. The concentrations used in a typical EPR experiment were as follows: $[NHPI]_0 = [Cu(NO_3)_2]_0 = 0.04$ M, T = 25 °C. The PINO signal lies between 3 and 4 signal lines of Mn(II) ($g_3 = 2.0314$, $g_4 = 1.9812$).

^1H NMR spectra were recorded on a 400 MHz spectrometer (Bruker BioSpin)with $CDCl_3$ as the solvent and tetramethylsilane as an internal standard.

3. Results and discussion

3.1. Catalytic oxidation of HMF to DFF

The oxidation reactions of HMF in acetonitrile in the presence of NHPI/metal salt catalytic systems were studied. The target oxidation product DFF had been isolated from the reaction mixture and characterized by elemental analysis and ^1H NMR spectra. The yields of DFF under various reaction conditions were presented in Table 1. The DFF yield depended largely on the nature of the metal cocatalyst. Ions of transition metals such as Co(II), Co(II), Mn(III), and V(IV), that are known as effective cocatalysts for the oxidation of alcohols using NHPI [18], displayed low to moderate activity in HMF oxidation (Entries 1–6). The yield of dialdehyde increased remarkably when $Cu(NO_3)_2 \cdot 3H_2O$ is used (Entry 8). When we utilized nitrates of other metals like Ca(II) or Sr(II) the reaction was very sluggish (Entries 9, 10). Low DFF yields were achieved when $CuCl_2$ or CuCl was employed instead of $Cu(NO_3)_2$ (Entries 7, 11). Oxidations proceeded smoothly without formation of observable amounts of 2,5-furandicarboxylic acid.

Table 1
The oxidation of HMF to DFF with oxygen in the presence of NHPI.[a]

Entry	Cocatalysts	T, °C	Time, h	Yield, %[b]
1	$Co(acac)_2$	75	8	26 (14)
2	$Co(acac)_3$	75	10	12 (8)
3	$Mn(acac)_3$	75	10	13 (8)
4	$VO(acac)_2$	50	6	4 (2)
5	$Co(acac)_3$	50	10	12 (7)
6	$Co(acac)_2$	50	10	7 (2)
7	CuCl	50	8	Traces
8	$Cu(NO_3)_2 \cdot 3H_2O$	50	7	71 (53)
9	$Ca(NO_3)_2$	50	12	Traces
10	$Sr(NO_3)_2$	50	14	Traces
11	$CuCl_2$	50	18	6 (2)

[a] Standard procedure: 1×10^{-3} M of HMF, 0.1×10^{-3} M of NHPI, and 0.02×10^{-3} M of cocatalyst in 2 ml of acetonitrile with $p(O_2) = 1$ atm.

[b] Determined by NMR. Numbers in parenthesis give the yield of DFF after its isolation by several times ofvacuum sublimation.

It was shown (Table 2) that the HMF oxidation by catalytic system NHPI/$Cu(NO_3)_2$ could be well carried out under low temperature (50 °C) and oxygen pressure (1 atm). No reactions took place in the presence of $Cu(NO_3)_2$ or NHPI alone (Entries 2, 3).

Obviously, the presence of both NHPI and $Cu(NO_3)_2$ was crucial for the observed synergistic effect. Oxidation occurred to some extent in the presence of N-acetoxyphthalimide (NAPI) instead of NHPI, but the activity of the catalytic system was lower than when NHPI is present (Entries 4 and 5).

The electronic properties of the substituents in the NHPI benzene ring provided the significant effect to the oxidation rate of benzyl alcohols in the presence of N-hydroxyphthalimide [24]. The N-hydroxytetraphenylphthalimide (NHTPPI) with $Cu(NO_3)_2 \cdot 3H_2O$ demonstrated the highest activity in HMF oxidation. Thus, the combination of $Cu(NO_3)_2$ with NHTPPI was the most effective one among tested catalytic systems.

3.2. Formation of PINO

The addition of the radical inhibitor 3,5-di-tert-butyl-4-hydroxytoluene to the reaction mixture (NHPI, $Cu(NO_3)_2 \cdot 3H_2O$ and HMF in acetonitrile) led to the appearance of the induction period. These observations suggested that the oxidation proceeded in a radical pathway. The generation of PINO by the reaction of the NHPI with the copper(II) under ambient conditions could be the most probable step in the present

Table 2
The initial rates of O_2 uptake in the NHPI/$Cu(NO_3)_2$ catalyzed oxidation of HMF.

Entry	N-hydroxyphthalimide catalyst[a]	Copper cocatalyst	Initial rate of oxidation, $W_{ox} \times 10^6\ M \cdot s^{-1}$[b]
1	None	None	Lower than 0.5
2	None	$Cu(NO_3)_2 \cdot 3H_2O$	Lower than 0.5
3	NHPI	None	14.5
4	NHPI	$Cu(NO_3)_2 \cdot 3H_2O$	135.0
5	NAPI[c]	$Cu(NO_3)_2 \cdot 3H_2O$	20.0
6	NHTPPI[d]	$Cu(NO_3)_2 \cdot 3H_2O$	245.0

[a] Standard procedure: 1×10^{-3} M of HMF, 0.1×10^{-3} M of NHPI-like catalyst, and 0.02×10^{-3} M of copper cocatalyst in 2 ml of acetonitrile were oxidized with O_2 at 50 °C and atmospheric pressure.

[b] Oxidation rates were calculated on a basis of oxygen uptake vs. time curves, obtained at a constant pressure and temperature (Fig. S1).

[c] N-acetoxyphthalimide.

[d] N-hydroxytetraphenylphthalimide.